RUBBER BLEND (ENR 25/NBR) BASED PRESSURE-SENSITIVE ADHESIVES

SOO KAI WAI

UNIVERSITI SAINS MALAYSIA

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RUBBER BLEND (ENR25/NBR) BASED PRESSURE-SENSITIVE ADHESIVES

by

SOO KAI WAI

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LIST OF ABBREVIATIONS AND SYMBOLS

ENR	Epoxidized natural rubber
h	Hour
kg	Kilogram
N	Newton
NBR	Nitrile-butadiene rubber
BPO	Benzoyl peroxide
PSA	Pressure sensitive adhesive
SMR	Standard Malaysian Rubber
ASTM	American Standard for Testing and Materials, USA
MPa	Megapascal
PET	polyethylene terephthalate
ZnO	Zinc oxide
MgO	Magnesium oxide
T_g	Glass transistion temperature
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectrocopy
ATR	Attenuated total reflection
CI	Coumarone–indene resin
G’	storage modulus
SIS	Styrene-isoprene-styrene
SBS	Styrene-butadiene-styrene

PIB	Polyisobutylene
BIMS	Brominated isobutylene- co-p-methylstyrene
BA	Butyl acrylate
MMA	Methyl methacrylate
PVA	Poly(vinyl alcohol)
EPDM	Ethylene-propylene-diene
SBR	Styrene-butadiene rubber

PEREKAT TEKANAN-PEKA BERASASKAN GAULAN GETAH

(ENR 25/NBR)

ABSTRAK

Dalam kajian ini, penyediaan dan pencirian perekat tekanan-peka gaulan getah asli terepoksida (ENR 25) / getah nitril butadiene (NBR) akan dibincangkan. Nisbah campuran getah telah ditetapkan pada 0, 20, 40, 60, 80, dan 100% daripada kandungan ENR 25. Zink oksida (ZnO) dan magnesium oksida (MgO) telah digunakan sebagai pengisi dalam penyediaan perekat komposit. Lima kandungan pengisi yang berbeza telah digunakan untuk penyediaan perekat, iaitu 10, 20, 30, 40 dan 50 phr. Benzoil peroksida (BPO) telah digunakan sebagai agent paut silang untuk menyediakan perekat paut silang. Penambahan kandungan benzoil peroksida adalah dalam julat 1-5 phr. Dalam sepanjang kajian ini, toluena telah digunakan sebagai pelarut. Coumarone-indene, resin petro dan rosin gam telah digunakan sebagai resin pelekit. Perekat dilitup mengikut ketebalan litupan 30, 60, 90, dan 120 mikron pada filem polietilena tereftalat (PET) dengan menggunakan penglitup tangan SHEEN. Sifat rekatan (kekuatan lekatan, kekuatan kupasan, dan kekuatan ricihan) perekat diukur dengan menggunakan mesin penguji rekatan Lloyd yang beroperasi pada 10-60 cm / min. Keseimbangan bengkak dalam toluena telah digunakan untuk mengukur kepadatan paut silang perekat. Keputusan kajian juga menunjukkan kelikatan perekat berkurangan dengan peningkatan peratus ENR 25 dan meningkat dengan kandungan pengisi. Keputusan telah menunjukkan bahawa peningkatan sifat rekatan, modulus simpanan dan modulus kehilangan untuk perekat paut silang dan perekat komposit. Perekat paut silang yang menunjukkan peratusan bengkak yang rendah akan mempunyai kandungan gel dan ketumpatan paut silang yang lebih tinggi. Termograf

TGA menunjukkan bahawa penambahahan ZnO, MgO dan BPO meningkatkan kestabilan terma untuk gaulan getah ENR25/NBR kepada pelbagai jenis darjah dan ia bergantung kepada kandungan pengisi ZnO, MgO and BPO. Termograf DSC menentukan keupayaan campuran untuk gaulan getah ENR25/NBR. Mikroskop Imbasan Elektron (SEM) menunjukkan kewujudan kegagalan perekat dan kegagalan kohesif pada perekat getah.

RUBBER BLEND (ENR 25/NBR) BASED PRESSURE-SENSITIVE ADHESIVES

ABSTRACT

In this study, the synthesis and characterization of epoxidized natural rubber (ENR 25)/ acrylonitrile-butadiene rubber (NBR) blend pressure sensitive adhesive (PSA) were presented. The blend ratio of ENR25/NBR was fixed at 0, 20, 40, 60, 80, and 100% of ENR 25 content. The zinc oxide (ZnO) and magnesium oxide (MgO) were used as a reinforcing filler to prepare the composite adhesive. Five different loadings, i.e. 10, 20, 30, 40 and 50 phr filler was used in the adhesive formulation. The benzoyl peroxide (BPO) is used as a crosslinking agent to prepare the crosslinked adhesive. The loading of benzoyl peroxide was varied from 1 to 5 phr. Toluene was used as solvent throughout the study. Coumarone-indene, petro resin and gum rosin were used as tackifiers. A SHEEN hand coater was used to coat the adhesive on polyethylene terephthalate (PET) at 30, 60, 90, and 120 μm coating thickness. Adhesion properties (loop tack, peel strength, and shear strength) of adhesives were measured using a Lloyd adhesion tester operating at 10–60 cm/min. Equilibrium swelling in toluene was used to measure the crosslinking density of the crosslinked adhesive. The results show that the viscosity of the adhesive decreases with increasing % ENR 25 and increase with the filler loading. The results also show that an increase adhesion properties, storage modulus and loss modulus for crosslinked adhesives and composite adhesives. Crosslinked adhesives which show lower percentage of swelling, produced higher percentage of gel content and have higher crosslink density. TGA thermograms show that addition of ZnO, MgO and BPO improved the thermal stability of ENR25/NBR rubber blend to different degrees depending on ZnO, MgO and BPO

loading. The DSC thermogram confirms the miscibility of the ENR25/NBR rubber blend. The SEM micrographs demonstrate the occurrence of cohesive and adhesion failure modes of the rubber adhesive.

CHAPTER 1 INTRODUCTION

1.1 General

In 19th century, glues originated from plants and animals (Pizzi and Mittal, 2003). Animal glues were mostly based on mammalian collagen which were the main protein of skin, bone and sinew, and the plant kingdom provided starches and dextrin from corn, wheat, potatoes and rice. Synthetic chemicals had largely taken over during 20th century (Comyn, 1997).

In the modern adhesives and sealants technology period, from the earliest day, the material that we called glues, gums and pastes, and finally, adhesives and sealants, are used interchangeably. For the most part it has a vain attempt, as most of the people so-called adhesives also serve as sealants, and all sealants have adhesive properties (Pizzi and Mittal, 2003).

An adhesive is a nonmetallic material that is applied between two solid surfaces to join them permanently by an adhesive bonding process (Ebnesajjad and Landrock, 2014). An adhesive is a substance forming a bond to each of the two parts when the final object consists of two section that are bonded together (Satas, 1982, Benedek, 2004). Adhesives working through adhesion phenomena, the adhesive fluid is transformed after bonding into a solid. Adhesion is difficult to define, and an entirely satisfactory definition has not been found. Traditionally, adhesion is defined as the phenomenon in which layers of contacting materials are held together by interfacial forces (Benedek and Feldstein, 2008a, Ebnesajjad and Landrock, 2014).

Today adhesives are used in all types of manufacture and in many cases have displaced other means of joining. It shows very obviously from home and office to the space shuttle, many products that we take for granted could never exist if it were not for adhesives (Comyn, 1997, Petrie, 2000). Adhesives is a material that can be designed with a wide range of strengths, from weak temporary adhesives (holding papers in place) to high strength structural systems (bond cars and airplanes). Adhesives compete with mechanical fastening systems such as nuts and bolts, rivets or welding and soldering in many industries (Connell et al., 1997, Dunn, 2010).

Adhesive bonding has advantages and disadvantages when compared to other types of bonding. Among the advantages include their ability to join any combination of similar or dissimilar materials and thin sheet materials (da Silva et al., 2011). Furthermore, an adhesive bond has a large stress bearing area. Besides that, adhesive bonding is often faster and cheaper than mechanical fastening (Petrie, 2000). Some disadvantages include the limitation of adhesives by their glass transition temperature and chemical degradation due to their service temperature ranges are less than for metal fasteners such as nuts, bolts, welds, staples and so on. Moreover, adhesives as a means of joining is that they are generally weakened by water and its vapour (Comyn, 1997).

There are several classification methods for adhesives. Adhesives may be broadly divided in two classes, namely structural and non-structural adhesives (Ebnesajjad and Landrock, 2014). Structural adhesives are expected to provide a bonds durable throughout the useful service life of a part. Moreover, the bonding for the structural adhesive bonding is for application in which adherents experience large

stresses up to their yield point (Dunn, 2010). Nonstructural adhesives form a bond simply by the application of light force to bond the adhesive with the adherent. Nonstructural adhesives bonding is applied to hold lightweight materials in place. Sometimes, it is called a "holding adhesive" for this type of adhesive. An examples of nonstructural adhesives are pressure sensitive tapes and packaging adhesives (Petrie, 2000).

Differential with other classes of adhesives, pressure sensitive adhesive (PSA) retain their fluid state after the bond is built. They remain in a permanently tacky state (Benedek, 2004). Such material has a capacity to achieve this instantaneous adhesion to most solid surfaces with the application of light pressure and can be debonded without leaving a residue of adhesive on the substrate. In the PSA technology, tack defines as the ability of the adhesive to form a bond with the surface of another material upon low contact pressure and short application time (Satas, 1982).

1.2 Problem Statement

The PSA industry is among the fastest growing in the adhesive market, making the search for new pressure sensitive products and applications highly competitive (Jovanović and Dubé, 2004). Although PSA products can be obtained by polymerization processes with the different base elastomer, much attention has recently been devoted to the utilization of more environmentally friendly rubber based adhesive. In addition, natural adhesives dominate the market nowadays, even in the most developed countries due to the natural rubber are less expensive than synthetic rubber and they perform the intended function (Pizzi and Mittal, 2003). Malaysia since 1970s was the largest producer of natural rubber in the world until late 1980’s (Hassan

et al., 2013). Natural rubber is used widely as a base elastomer in PSA field will develop rubber industry in Malaysia.

Recently, acrylic-based emulsion availability issues are prompting more and more formulators to go back to natural rubber based PSA from a performance, availability and economics stand point (Raja et al., 2013b). According to Fujita et al. (1998), natural rubber based PSA has a very long history and it has been widely used in the greatest deal of all of the PSA in Japan and cannot be completely replaced by acrylic polymers. Typically natural rubber has many attractive properties which including low cost (Pongtanayut et al., 2013), low hysteresis (Teh et al., 2004), high resilience (Chuayjuljit et al., 2015) and excellent dynamic properties (Wan et al., 2009).

Nowadays, adhesives are important materials in many industries and services. Owing to wide range of applications involved, the PSA formulated should withstand different environmental and physical conditions. PSA have been formulated with major components such as polymer, tackifying resins and additives (filler, plasticizers, stabilizers etc.) to improve tack and processing characteristics (Raja et al., 2013a). Tables 1.1 and 1.2 respectively show the previous studies of PSA and blended PSA by other researchers. The Tables show that limited literature regarding the natural rubber based PSA. The Tables also indicate that the previous work in this area is focused on synthesizing adhesive from the single component system and most of the adhesives are prepared from acrylic rubber. According to Benedek (2004), the common acrylic PSA is not tacky enough and special acrylic PSA is not cohesive enough. Besides, the tack of unformulated acrylic PSA is lower than that of tackified rubber based PSA.

Table 1.1: Previous studies of PSA by other researchers

Polymer	Tackifier	Filler	Crosslinking agent	Reference
Acrylic	Rosin		Benzoyl peroxide	Abderrahmen et al. (2011)
Styrenic	Hydrocarbon resin (Piccotac® 1095, Piccotac® 9095, Piccotac® 8095, Piccotac® 7590-C, Piccotac® 6095-E)			O'Brien et al. (2007)
Acrylic	Diethylene glycol ester of hydrogenated rosin			Zhang et al. (2016)
Acrylic		Montmorillonite (MMT) clay	Dibenzoyl peroxide	Kajtna and Šebenik (2009)
Acrylic		Montmorillonite (MMT) clay		Li et al. (2004)
Acrylic	Hydrogenated rosin epoxy methacrylate			Do et al. (2008)
Acrylic			Benzophenone	Do et al. (2006)
Acrylic		Montmorillonite (MMT) clay	Azobisisobutyronitrile (AIBN), 4-acryloyloxybezophenone	Kajtna et al. (2014)
Acrylic			Aluminum acetylacetonate	Murakami et al. (2011)
Acrylic			N,N,N',N'- tetraglycidyl-m-xylenediamine	Pang et al. (2013a)
Styrene-butadiene-styrene (SBS)	Hydrogenated rosin		Benzoyl peroxide, Trimethylolpropane tris-(3-mercaptopropionate)	Wu et al. (2010)

Table 1.1 Continue

Acrylic			Polyisocyanate	Asahara et al. (2003)
Acrylic			2,2'-azobisisobutyronitrile, 2,2-Dimethoxy-1,2-diphenylethanone	Joo et al. (2007)
Acrylic			2,2'-azodiisobutyronitrile, Aluminum acetylacetonate	Kowalski et al. (2013)
Acrylic		Silica	N,N'- azobisisobutyronitrile, 1-hydroxycyclohexylphenyl ketone	Pang et al. (2013b)
Polyisobutylene (PIB)		Halloysite, Silica		Kostyuk et al. (2015)
Acrylic		Silica		Shanks et al. (2011)
Acrylic		Iron carbide	2,2'-azo-bis-diisobutyronitrile, Titanium acetyloacetonate	Czech et al. (2013a)
Acrylic		Silica, Montmorillonite	Benzoyl peroxide	Patel et al. (2006)
Styrene-isoprene-styrene (SIS)	Hydrocarbon resin (C-100R)		Hydrogen peroxide	Zhao et al. (2014)
Acrylic			Azobisisobutyronitrile, Benzoine isopropylether, 1-Hydroxycyclohexyl acetophenone, 1,1,1-Trichloro acetophenone, 2-Hydroxy-2-methyl-1-phenylpropanone, Benzildiethyl phosphineoxide	Czech et al. (2013b)

Table 1.1 Continue

Styrene-grafted natural rubber (SNR), Deproteinized natural rubber (DPNR)	Gum rosin, Petro resin, Coumarone-indene resin (CI)		Azura et al. (2014)
Standard Malaysian Rubber (SMR L), Epoxidized natural rubber (ENR 25, ENR 50)	Coumarone-indene resin (CI)/Gum rosin		Musa et al. (2015)
Brominated isobutylene- co-p-methylstyrene (BIMS)	Phenolic Resin		Kumar et al. (2008)
Epoxidized natural rubber (ENR 50)	Gum rosin		Khan et al. (2013)
Epoxidized natural rubber (ENR 50)	Petro resin		Khan and Poh (2012a)
Standard Malaysian Rubber (SMR L)	Gum rosin, Petro resin		Poh and Yong (2008)
Epoxidized natural rubber (ENR 25, ENR 50)	Coumarone-indene resin (CI)	Calcium carbonate	Poh et al. (2008a)
Epoxidized natural rubber (ENR 25)	Petro resin	Magnesium oxide (MgO)	Poh and Gan (2010)
Epoxidized natural rubber (ENR 25, ENR 50)	Coumarone-indene resin (CI)		Poh and Kwo (2007)
Epoxidized natural rubber (ENR 25, ENR 50)	Gum rosin, Petro resin, Coumarone-indene resin (CI)		Poh and Yong (2009b)
Epoxidized natural rubber (ENR 25)	Coumarone-indene resin (CI)	Zinc oxide (ZnO)	Poh and Chow (2007)
Styrene-isoprene-styrene (SIS)	Petroleum resin		Sakaguchi et al. (2010)

Table 1.1 Continue

Standard Malaysian Rubber (SMR L)	Coumarone-indene resin (CI)		Benzoyl peroxide	Poh and Cheong (2012)
Epoxidized natural rubber (ENR 25)	Coumarone-indene resin (CI)			Khan and Poh (2011a)
Epoxidized natural rubber (ENR 50)	Coumarone-indene resin (CI)		Benzoyl peroxide	Poh and Lim (2014)
Standard Malaysian rubber (SMR 10)	Coumarone-indene resin (CI)			Poh and Chang (2006)
Epoxidized natural rubber (ENR 25)	Gum rosin, Petro resin		Benzoyl peroxide	Poh and Suid (2013)
Epoxidized natural rubber (ENR 25, ENR 50)	Coumarone-indene resin (CI)	Silica		Khan and Poh (2010b)
Epoxidized natural rubber (ENR 25)	Coumarone-indene resin (CI)	Barium chloride		Poh and Lai (2010)
Standard Malaysian rubber (SMR 10)	Coumarone-indene resin (CI)	Sodium sulfate		Khan et al. (2010)
Standard Malaysian rubber (SMR 20)	Coumarone-indene resin (CI)			Poh and Chee (2007)
Styrene-butadiene rubber (SBR)	Gum rosin, Petro resin			Poh et al. (2010)
Epoxidized natural rubber (ENR 25)	Gum rosin	Kaolin		Poh and Chew (2009)
Epoxidized natural rubber (ENR 50)	Coumarone-indene	Magnesium oxide (MgO)		Poh and Saari (2011)
Epoxidized natural rubber (ENR 25)	Gum rosin			Poh and Khan (2014)

Table 1.2: Previous studies of blended PSA by other researchers

Polymer	Tackifier	Filler	Crosslinking agent	Reference
Styrene isoprene styrene (SIS) /styrene isoprene (SI)				Derail et al. (2004)
Butyl acrylate (BA) /Methyl methacrylate (MMA)			Allyl methacrylate	Qie and Dubé (2010)
Styrene-butadiene rubber /polychloroprene	Hydrocarbon resin (Kristalex F100, Kristalex 3115, Kristalex 5140, Piccolastic D125)			Teresa et al. (1997)
Styrene-vinylacetate copolymer latex (S-VAc) /Natural rubber latex (NRL)	Nonyl phenol ethoxylate (NPE)			Magida et al. (2009)
Epoxidized-low protein skim rubber (E-LPSR) /Poly(vinyl alcohol) (PVA)	Coumarone-indene resin (CI)		Hydrogen peroxide	Riyajan et al. (2013)
Saponified-low protein skim rubber (S- LPSR) /Poly(vinyl alcohol) (PVA)	Coumarone-indene resin (CI)	2,6-di-t-butyl-4-methylphenol (BHT), 4,4'-thio bis(6-tert-butyl-3-methylphenol), 2,2'-methylene bis(4-ethyl- 6-tert-butylphenol)		Riyajan and Pheweaw (2012)

Table 1.2 Continue

Epoxidized natural rubber (ENR 25) /Ethylene-propylene-diene (EPDM)	Coumarone-indene resin (CI)	Benzoyl peroxide	Poh and Teh (2014)
Standard Malaysian rubber (SMR 10) /Epoxidized natural rubber (ENR 25), Standard Malaysian rubber (SMR 10) / Epoxidized natural rubber (ENR 50), Epoxidized natural rubber (ENR 25) /Epoxidized natural rubber (ENR 50)	Coumarone-indene resin (CI)		Poh and Lim (2008)
Ethylene-propylene-diene (EPDM) /Standard Malaysian Rubber (SMR L)	Coumarone-indene resin (CI)		Poh et al. (2013)
Styrene-butadiene rubber (SBR) /Standard Malaysian Rubber (SMR L)	Phenol-formaldehyde resin		Poh and Ong (2007)
Epoxidized natural rubber (ENR 25) /Styrene-butadiene rubber (SBR)	Coumarone-indene resin (CI)		Poh and Chee (2015)
Poly (vinylpyrrolidone) (PVP) /Acrylic			Taghizadeh et al. (2009)
Acrylonitrile-butadiene rubber (NBR) /Standard Malaysian Rubber (SMR L)	Coumarone-indene resin (CI)		Poh and Lamaming (2013)

It is well known that polymer blending is the opportunity to develop materials with new or improved properties at reduced material cost. Natural rubber is a polyisoprene which has good tack properties but normally does not have very high strength. The drawbacks of natural rubber is ease of degradation in outdoor environments due to it being a polyunsaturated isoprene compound. Therefore, epoxidation has been applied to solve this problem (Riyajan et al., 2013). The mechanical properties of natural rubber are generally superior to those of synthetic rubber. However, natural rubber cannot compete with the specialty synthetic elastomers with regard to such properties as gas permeability and oil resistance (El-Sabbagh and Yehia, 2007). The blending of epoxidized natural rubber (ENR 25) with nitrile rubber (NBR) is intended to produce an adhesive with good in oil resistant properties.

Tables 1.1 and 1.2 also show that most of the previous report of crosslinked adhesives are focused on the single rubber adhesives and the previous studies of crosslinked rubber blend based adhesives are scarcely reported. Crosslinking is an important method to improve the PSA adhesion properties. Crosslinking is affected most of the mechanical properties of the PSA, including increasing its cohesive strength (Czech, 2006). The polymer in PSA is a viscoelastic material that is permanently as well as aggressively tacky. Besides, it has enough cohesive strength and elasticity to be cleanly removed from a substrate surface. Therefore, the degree of crosslinking is one of the key features to control the balance between cohesive and adhesive strength of the adhesive (Bunker et al., 2003).

Besides, Tables 1.1 and 1.2 also indicate that the systematic research involving the use of filler in the adhesives are not widely carried out and most of the filler filled adhesives are prepared from layered silicate or clay. The combination of organic polymers and inorganic particles into composites have attracted considerable attention in recent years. This materials offer the prospect of new synergetic properties that originate from their organic and inorganic components (Wang et al., 2009). According to Li et al. (2004), loading of filler in the adhesive system yielded a product with a good balance between holding strength and tack properties. In view of the importance of the filler on the adhesion property of the rubber based adhesives, thus the effect of the introduction of the filler in the rubber blend adhesive has been carried out.

1.3 Objectives

i. To study the effects of blend ratio on the adhesion properties and thermal properties of ENR-25/NBR based pressure sensitive adhesives (PSA).
ii. To study the effects of crosslinking agent on the adhesion properties and thermal properties of ENR-25/NBR based pressure sensitive adhesives (PSA).
iii. To study the effects of zinc oxide (ZnO) and magnesium oxide (MgO) on the adhesion properties and thermal properties of ENR-25/NBR based pressure sensitive adhesives (PSA).
iv. To investigate the effect of zinc oxide on the adhesion properties and thermal properties of benzoyl peroxide cured ENR-25/NBR based pressure sensitive adhesives (PSA).

1.4 Scope of Study

This research is to portray the possibility of producing a new rubber blend based PSA based on ENR 25/NBR blends. The tackifiers used in this study are coumarone-indene, petro resin and gum rosin. In the first part of the study, the influence of rubber blend ratios on the adhesive performance is investigated. The second part of the study is focused on the performance of ENR 25/NBR blend adhesive by using different type of fillers (ZnO and MgO) with the coumarone-indene resin, petro resin and gum rosin tackifiers. Lastly, the aim of the study is focused on the performance of benzoyl peroxide crosslinked ENR 25/NBR blend adhesive that prepared with the different type of tackifiers as well as the crosslinked ENR 25/NBR blend adhesive with the ZnO loading. The study is mainly focused on the influence of coating thickness, testing rate and testing angle on the adhesion property of ENR 25/NBR based adhesives. Eventually, the study is also focused on understanding the interaction between rheological properties of the PSA bulk rubber with adhesion property.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction of Pressure Sensitive Adhesive (PSA)

In 1925, it was generally considered to be the birth date of the pressure sensitive tape industry. Both cloth-backed surgical tapes and cloth-backed friction tape for use by electricians were in limited use prior to the time. Both were apparently tried as masking tapes for the new two-toned automobiles, but failed to strip clean and resist paint penetration. A crepe paper backing that impregnated with animal glue and glycerin and also coated with a pressure sensitive adhesive (PSA) was developed in 1925 (Clark et al., 1954, Pizzi and Mittal, 2003).

PSA is an adhesive that remains sticky when dried or cured and at the same time, PSA is capable of bonding to surfaces simply by the application of light pressure (Satas, 1982, Czech, 2007). During the bonding process, PSA does not go through any chemicals reaction or physical transformation (Fujita et al., 2000, Taghizadeh and Ghasemi, 2010). Moreover, PSA is designed with a balance between flow and resistance to flow (Feldstein et al., 2015). In addition, tack, peel strength and shear strength are usually used to evaluate its performance (Kostyuk et al., 2015, Creton, 2003).

Generally, PSA is also semi solid materials composed of a lightly crosslinked high molecular weight polymer that is the backbone of the structure. Besides, it is also composed of one or more low molecular weight additives that generally dilute the entanglement network and also adjust the viscoelastic properties (Lindner et al., 2006). In addition, PSA can be single polymer or multi component types such as elastomer

adding with tackifiers and other additives. Moreover, PSA has low glass transition temperature (Li et al., 2001, Lopez et al., 2011b).

In general, PSA can be divided into three groups, namely solvent-based, hot-melt and water-based adhesives (Pizzi and Mittal, 2003). Solvent-based adhesive is synthesized in solvent solution and dried to form the adhesive film (Abderrahmen et al., 2011). Solvent–based adhesive typically has been the preferred choice of converters due to the ease of application and desirable to balance the PSA performance properties. For example, solvent–based rubber resin PSA possess aggressive adhesion, good cohesion and water resistance when used as fully commercial products (Benedek, 2004). According to Ebnesajjad and Landrock (2014), solvent–based adhesive usually makes bonds that is more water resistance and has higher tack and early strength than water–based adhesive. Besides, solvent–based adhesive also wets oily surfaces and some plastics considerably better than water–based adhesive (Ebnesajjad, 2010).

Water-based adhesive ingredients are polymerized in water, applied to the film and dried to create a functional adhesive (Rolando, 1998). Abderrahmen et al. (2011) stated that the water-based PSA is composed of polymers in emulsion with the solid content from 40 to 60 % wt. Besides, hot-melt adhesive is a solvent free adhesives. This means that hot-melt adhesive is composed of thermoplastic polymers and applied as a 100% solids (Gierenz and Karmann, 2008). This thermoplastic adhesive requires heating to be processed and it is based on thermoplastic rubbers use temperature (Benedek, 2004). Abderrahmen et al. (2011) stated that hot-melt adhesive involves high viscosity processing conditions. Table 2.1 exhibits the chemical composition, advantages and limitation of solvent-based, water-based and hot-melt adhesive.

Table 2.1: The advantages and limitation of solvent-based, water-based and hot melt adhesive

Pressure Sensitive Adhesive	Chemical Composition	Advantage	Limitation
Solvent-Based	Rubber/resin, acrylics, silicones	Good adhesion to non -polar substrate Good key on certain plastics Form homogenous films Drying quickly	Relatively low solid content Flammability Difficult cleaning
Water-Based	Acrylics, natural and synthetic rubber, ethylene–vinyl acetate copolymer	Good adhesion to polar substrate Good heat and ageing resistance Environment friendly High solid content Easy cleaning	Poor adhesion on non - polar substrates Presence of surfactant Drying slowly Require heat to dry
Hot-Melt	Block copolymers, acrylics	Environment friendly 100% active Fast setting	High equipment costs Able to melt the substrate Thermal degradation Difficult to clean Require heat

Source: (Doyle and O'Quinn, 2011, Jovanović and Dubé, 2004)

There are large variations of elastomers have been used as PSAs, namely natural rubber PSA, acrylic PSA and silicone PSA. The first material to acquire common use was a natural rubber PSA. Normally, natural rubber is obtained as natural latex. The latex is coagulated and then the rubber is usually smoked to eliminate bacteria and fungi. Then, the mechanically smoked rubber is dissolved in solvent, mixed with tacktifier and packaged (Bhowmick and Stephens, 2000). Natural rubber PSA is the basic for all of the early PSA products. One of the primary attributes of natural rubber PSA is due to low cost and high peel strength when formulated in proper. Natural rubber PSA are widely employed in pressure sensitive adhesive tape (PSAT) applications because of the excellent removability after painting and baking (Pocius, 2002).

The first use of acrylic PSA is intended to bond glass, paper or material to metals. It is illustrated as an adhesive which is applied either as a film placed between the adherents or a 10% solution in acetone (Benedek and Feldstein, 2008b). Acrylic acid is employed to improve adhesion and optimize the elongation properties. Acrylic PSA provides more latitude for formulation and optimization (Patel et al., 2006, Kowalski et al., 2013). Even though some acrylic rubbers have been employed successfully as PSA in many industries, but a property inherent to all acrylic PSA has negatively impacted tack and adhesion performance (Czech, 2005). On the other hand, PSA based on acrylic random copolymers do not allow such a precise control of the structure (Lindner et al., 2006).

Silicone PSA are flexible and water repellant viscoelastic rubbers. Besides, silicone PSA also has low surface tension and can spread easily on surfaces. Silicone

PSA is often employed to provide high cohesive strengths at extreme temperatures or splice low surface energy materials. Silicone PSA is particularly useful as the adhesive for electrical insulating tapes and medical applications. Silicone are by far the most expensive of the base elastomers used in PSA (Tolia and Kevin Li, 2012).

2.2 Rubber Based Pressure Sensitive Adhesive (PSA)

Since 1845, natural rubber based PSA has been employed for medical applications when used for improved adhesive plaster using India rubber, pine gum and turpentine (Raja et al., 2013b). Therefore, additional developments has been following concentrated on medical applications. Natural rubber is the first base polymer that early used in PSA field for the manufacture medical plasters. Afterwards, the use, formulation and application of rubber based PSA is widely studied by scientist (Pizzi and Mittal, 2003).

Generally, natural rubber based PSA is less expensive and typically affected by oxidation and ultraviolet light. But, it is still designed for general purpose applications. For instance, removable rubber based PSA tend to increase in adhesion throughout the life of the label and could possibly become permanent (Benedek and Feldstein, 2008b, Raja et al., 2013b).

Natural rubber alone has a low adhesion property to the substrate therefore in formulating a rubber based PSA with a desired adhesion properties, it is necessary to add tackifying resin into the system (Benedek and Feldstein, 2008b). In the formulation, natural rubber provides the elastic component, whereas low molecular weight tackifying resin provides a viscous component. In addition, the good

compatibility of natural rubber with different tackifiers allows an easy adjustment for the balance of adhesion and cohesion properties of the PSA (Pizzi and Mittal, 2003, Benedek and Feldstein, 2008a).

2.3 Natural Rubber

Natural rubber is produced from milky white fluid which is collected by cutting narrow strips from the bark of the rubber tree *Havea Brasiliensis* (Cheremisinoff, 1996, Kohjiya and Ikeda, 2014). This milky white fluid is called latex (Pocius, 2002, Bhowmick and Stephens, 2000). In 1913, rubber plantation grew rapidly in Asia and exceed the production of wild rubber from Brazil. Since then, south-east Asia has remained the predominant natural rubber producing region. It accounted approximately 80% of the total production (Barlow, 1993).

Natural rubber contains approximately 30% to 40% of solids and 55 % to 60% of water. Besides, it gives a solid substance containing about 93 to 95 wt% of cis-1,4-polyisoprene on coagulation or evaporation to dryness while the balance being water and non-rubbery substances such as sugars, minerals, proteins and sterols (Yoksan, 2008, Angnanon et al., 2011). Figure 2.1 exhibits the polymer chain of natural rubber. Chemically, natural rubber is linear, long chain polymer with repeating isoprenic units (C_5H_8) (Brinson and Brinson, 2008, Barlow, 1993).

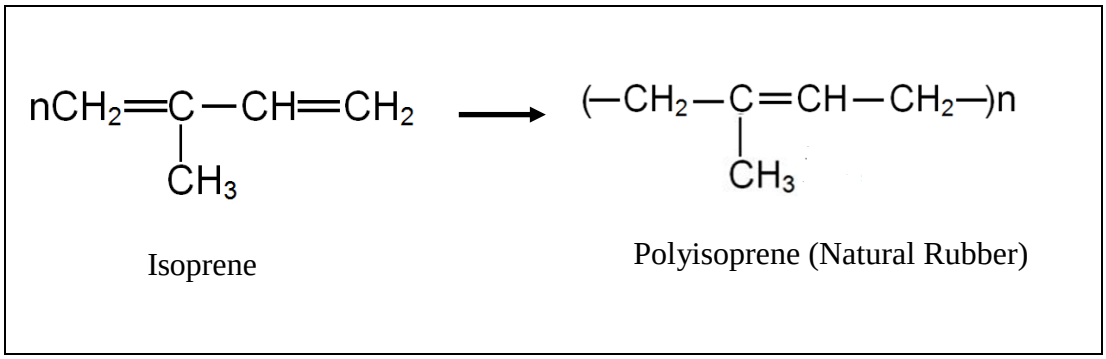

Figure 2.1: Polymer chain of natural rubber

Source: (Moore and Stanitski, 2014)

Natural rubber is composed of molecules of different sizes. The weight average molecular weight of natural rubber is ranging from 30,000 to 10,000,000. Natural rubber is stable below 200°C and decomposition significantly into smaller fragments which takes place at 290-300°C (Kohjiya and Ikeda, 2014). Besides, the gel content of raw natural rubber which has been stored for some time is much higher. It is called as macrogel and responsible for the increased viscosity during storage. The presence of certain active chemical groups such as carbonyl groups on the rubber chain is presumed to generate the production of branched chains (Barlow, 1993, De and White, 2001).

Natural rubber is a derived polymer which possesses the properties such as highly elastic, water vapor resistant and hydrophobic. In addition, natural rubber is established to perform various superior properties like improved wet grip and rolling resistance, coupled with high strength and low gas permeability. Besides, natural rubber is a crucial raw material for manufacturing several industrial products which ranging from medical devices and personal protective equipment to aircraft tires (Pal et al., 2010, Chamnanvatchakit et al., 2015).

2.3.1 Epoxidized Natural Rubber

Technology of epoxidized natural rubber (ENR) was developed when natural rubber reacted with a peroxy acid since 1922. Afterwards, a number of conflicting reports have been published on the preparation and properties of ENR. As a result of the oil crises in 1970, there was a renewed interest in the chemical modification of natural rubber to form other polymeric materials. Epoxidation was an attractive path because of the relatively low cost of the reagents involved, simple reaction procedure and the reaction can be carried out in the latex phase (Ismail et al., 1997, Hashim et al., 2002).

The ENR is a chemically modified form of natural rubber (cis-1, 4-polyisoprene) in which epoxide groups are incorporated by reacting natural rubber latex with peracetic acid. The isoprene and epoxidized isoprene act as monomer units that are randomly distributed along the polymer (Ismail et al., 2001, Chuayjuljit et al., 2006). The properties of ENR are quite different from natural rubber as epoxide groups substitute the unsaturated double bonds. Figure 2.2 exhibits the backbone double bonds of natural rubber are converted into epoxides (Davey and Loadman, 1984, Chamnanvatchakit et al., 2015).

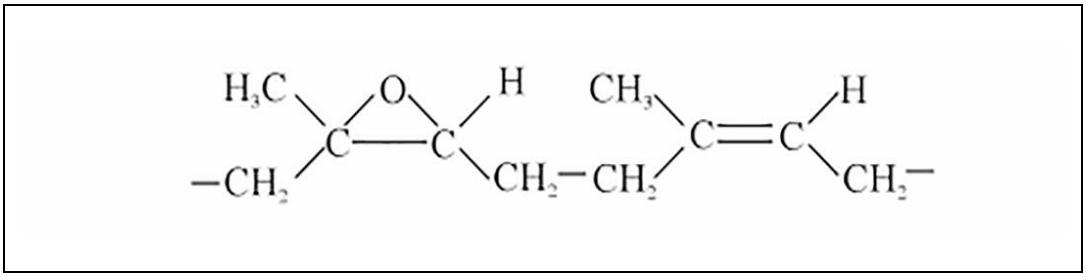

Figure 2.2: Chemical structure of epoxidized natural rubber

Source: (Gelling, 1991)

The limitation of natural rubber is ease of degradation in outdoor environments due to it being a poly unsaturated isoprene compound (Riyajan et al., 2013). Hence, epoxidation has been implemented to try to solve this issue. Various degree of epoxidation of natural rubber is commercially available. For examples, the isoprene units in the polymer chain are 25%, 50% and 75% epoxidized in ENR-25, ENR-50 and ENR-75, respectively (Hamzah et al., 2012). Commercially, more epoxide group content means more expensive ENR costs. Therefore, ENR 70 is seldom employed as an adhesive or sealant compared to those of ENR 25 and ENR 50 for the commercial purposes (Cizravi et al., 1999, Ismail et al., 1998). In addition, the properties of ENR change gradually with the epoxide level (Harun and Chan, 2016, Chamnanvatchakit et al., 2015). Swelling resistance and gas impermeability will be improved with increasing epoxide level. On contrary, resilience will be decreased (Baker et al., 1985, Roux et al., 1967).

The ENR owns high strength that can be improved by increasing the epoxide contents which mostly in between 25 and 50 mole %. This is due to its ability to comprise higher glass transition temperatures and solubility parameter. Natural rubber latex can be epoxidized to over 75 mol% without the formation of secondary ring opened structures if under carefully controlled conditions of reaction temperatures and acid concentration (Gelling, 1991).

Generally, the glass transition temperature and solubility parameter distinction influence the physical properties of ENR. On the other hand, the extent of epoxidation is controlled by the reaction temperature and reaction time. Moreover, epoxidation will affect an increase in the polarity, oil resistance but a decrease in gas permeability of

natural rubber (Zurina et al., 2007, Musa et al., 2015). Upon epoxidation, oxygen is small enough to fit into the crystal lattice with only minor geometrical rearrangements. Therefore, ENR can still undergo strain crystallization. Due to this, ENR can maintain the superior tensile properties of natural rubber (Davies et al., 1983, Harun and Chan, 2016).

2.4 Synthetic Rubber

Since World War I, synthetic rubber has been competing with natural rubber for world market share (Yahya et al., 2011). As highly profitable crop, the continuous production of natural rubber has secured its market position despite the substantial resources from synthetic rubber industry. Synthetic rubber and resin modified phenolic are employed to bond aluminium sheets into billets from which aeroplane propeller was carved during World War II. In 1947, the most successful widely known product of the new technology is the automotive bonded brake lining (Wellhausen and Mukunda, 2009).

Nowadays, about one-third of the adhesives which are used in the world are made from natural or synthetic rubber. In fact, synthetic rubber is mainly synthesised from petroleum by products. Synthetic rubber is a convenient term for any material which possesses the properties of a rubber but established from other than natural source. For many years, a synthetic version of natural rubber has been available with the same chemical formula but it has not displaced the natural form (Simpson, 2002, Alwaan, 2014).

Synthetic rubber is employed in place of natural rubber in many cases particularly when improved material properties are necessary. Natural rubber is poor

in chemical resistance and processing ability. Synthetic rubber is more resistant to oil and has better aging and weathering characteristics if compared to natural rubber. Besides, synthetic rubber is good resilience over a wider temperature range (Mrpra, 1989, Yahya et al., 2011).

Generally, the synthetic rubber was mainly divided into two groups, namely general purpose and special purpose (Visakh et al., 2013). Basically, general purpose synthetic rubber is called as hydrocarbon rubber. These include styrene butadiene, poly-butadiene, polyisoprene and so on (Khan and Poh, 2011c). In fact, general purpose synthetic rubber is contained substantial chemical unsaturation in their backbones "diene" that made them to be more susceptible to attack by oxygen. On the contrary, special purpose rubber has inherent characteristics such as ozone resistance, oil resistance and high temperature resistance which determined by the repeating units (Pizzi and Mittal, 2003).

The PSA is possibly the most common adhesive found in consumer products among the various group of adhesives. Synthetic rubber for PSA is available as elastomers and viscous components. The synthetic rubber industry produce lots of different synthetic rubbers to reflect the different applications and the wide range of requirements from the market. Synthetic rubber are preferred adhesive materials for employed in commercial PSA products because they exhibit excellent performance (Kowalski et al., 2013, Benedek, 2004).